

Chapter 4

Elementary Reactions

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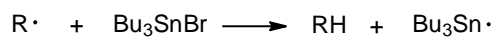
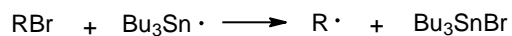
I. Introduction

An elementary reaction is one that has no intermediates. Every reaction that forms an intermediate actually is a combination of two or more elementary reactions. Where radicals are concerned, an elementary reaction either creates a radical from a nonradical, transforms one radical into another, or causes a radical to disappear.^{1,2}

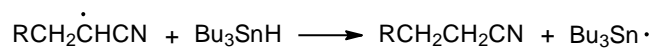
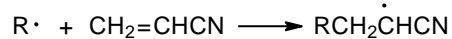
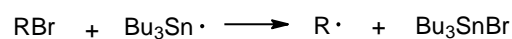
For chain reactions the propagation phase always contains at least two elementary reactions (Scheme 1). Nonchain reactions are similar in that they also contain at least two elementary reactions (Scheme 2). The elementary reactions upon which the free-radical chemistry of carbohydrates is based are listed in a general form in Table 1.^{1,2} Specific examples are given in the discussion of each reaction that takes place in this chapter. In describing these reactions the term “car-

Scheme 1

simple reduction: two elementary reactions

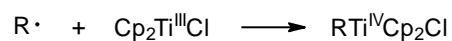
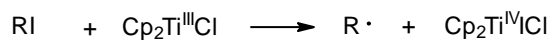


radical addition: three elementary reactions



Scheme 2

two elementary reactions: both electron-transfer



three elementary reactions: two electron transfer and one cyclization

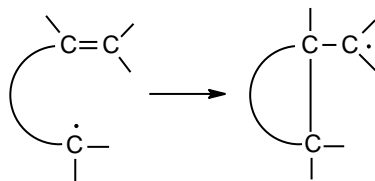
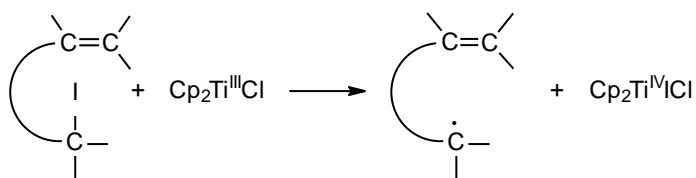


Table 1. Elementary Radical Reactions

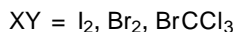
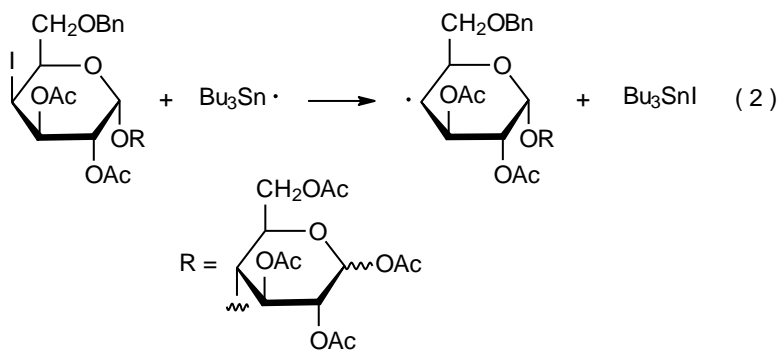
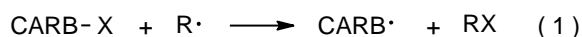
<u>Reaction Description</u>	<u>Reaction Equation</u>
atom abstraction (B is a single atom.)	$A\cdot + B-C \longrightarrow A-B + C\cdot$
group abstraction (B is a group of atoms.)	$A\cdot + B-C \longrightarrow A-B + C\cdot$
addition to a compound with a multiple bond	$A\cdot + B=C \longrightarrow A-B-C\cdot$
addition that produces a hypervalent atom	$A\cdot + \begin{array}{c} \ddot{B} \\ \\ - \end{array} \longrightarrow \begin{array}{c} \ddot{B} \\ \\ A \end{array}$
cyclization (internal addition)	$\begin{array}{c} B=C \\ \curvearrowright \\ A\cdot \end{array} \longrightarrow \begin{array}{c} B-C\cdot \\ \\ A \end{array}$
homolytic β -fragmentation	$A-B-C\cdot \longrightarrow A\cdot + B=C$
heterolytic β -fragmentation	$A-B-C\cdot \longrightarrow A^{\ominus} + {}^{\oplus}B-C\cdot$
α -fragmentation	$\begin{array}{c} \ddot{B} \\ \\ - \end{array} \longrightarrow A\cdot + \begin{array}{c} \ddot{B} \\ \\ - \end{array}$
bond homolysis	$A-B \longrightarrow A\cdot + \cdot B$
electron capture by a radical	$A\cdot + e^{\ominus} \longrightarrow A^{\ominus}$
electron donation by a radical	$A\cdot \longrightarrow A^{\oplus} + e^{\ominus}$
radical combination	$A\cdot + \cdot B \longrightarrow A-B$
disproportionation	$A\cdot + HB-C\cdot \longrightarrow AH + B=C$
migration	$A-B-C\cdot \longrightarrow \cdot B-C-A$

bohydrate radical" (CARB·) refers to a radical centered on one of the atoms, usually carbon, in a carbohydrate.

II. Atom Abstraction

A. Halogen-Atom Abstraction

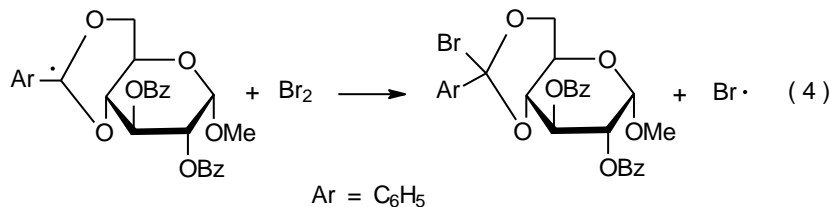
Halogen-atom abstraction can take place both in forming a halogenated carbohydrate and in removing a halogen atom from such a compound. When abstraction is from a halogenated carbohydrate, it produces a carbohydrate radical (eq 1). The abstracting radical typically is tin-centered or silicon-centered. In the reaction shown in eq 2, for example, a carbohydrate radical forms when a tin-centered radical abstracts an iodine atom from a deoxyiodo sugar.³ Abstraction that generates a halogenated carbohydrate takes place when I₂, Br₂, or another halogen-atom donor reacts with a carbohydrate radical (eq 3). Equation 4 describes a reaction of this type.⁴



B. Hydrogen-Atom Abstraction

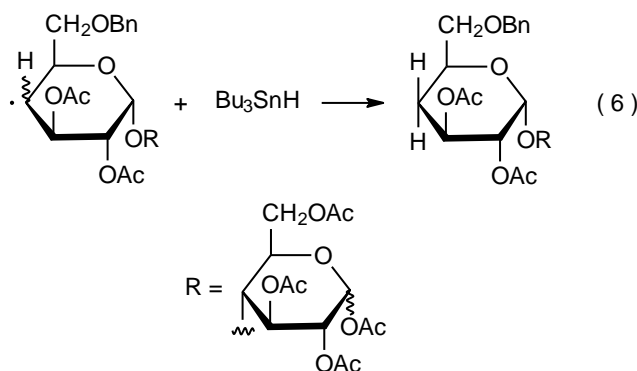
Hydrogen-atom abstraction is an elementary reaction that permeates the free-radical chemistry of carbohydrates. Because it is the final propagation step in many chain reactions, hydrogen-atom abstraction often converts a carbon-centered radical into a stable product. The

hydrogen-atom donor in such reactions usually is a tin or silicon hydride, but sometimes a thiol or selenol serves in this role (eq 5). The final step in the simple reduction shown in eq 6 is a typical, hydrogen-atom abstraction reaction.³



R[·] = a carbohydrate radical

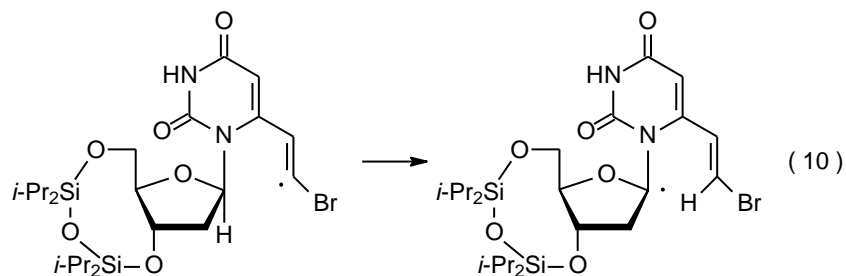
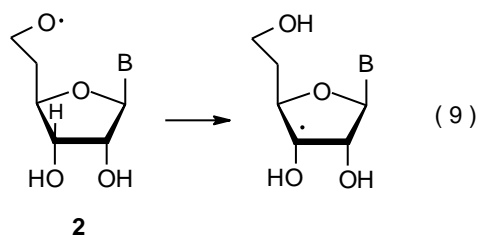
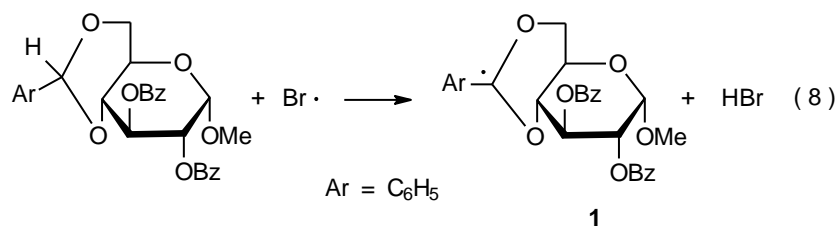
HX = a hydrogen donor, usually Bu₃SnH
or (Me₃Si)₃SiH but sometimes
(C₆H₅)₃SnH, C₆H₅SH, or C₆H₅SeH



X = Br, Cl, C, O, S

Carbohydrates also can serve as hydrogen atom donors (eq 7). A radical centered on a bromine, chlorine, or oxygen atom (and, sometimes, on a sulfur or carbon atom) is able to abstract a hydrogen atom from a carbohydrate in an elementary reaction that can be highly regioselective. For intermolecular reactions this selectivity is due to radicals preferentially abstracting the hydrogen atoms that produce the most stable carbon-centered radicals. In the reaction shown in eq 8, for example, the bromine atom abstracts only the hydrogen atom that produces the highly resonance-stabilized radical **1**.⁴

If a radical is centered on an oxygen or carbon atom in a carbohydrate, internal abstraction becomes a possibility. Such abstraction is regioselective not only because a more stable radical is being produced but also because the radical center is able easily to come within bonding distance of a limited number of hydrogen atoms (sometimes only one). In the reaction shown in eq 9, the only hydrogen atom abstracted is the one that is 1,6-related to the radical center.⁵ Although an oxygen-centered radical (e.g., **2** in eq 9) is reactive enough to abstract a hydrogen atom from any carbon-hydrogen bond in a carbohydrate,⁶ only the most reactive carbon-centered radicals (e.g., primary and vinylic ones) are capable of such reaction (eq 10).⁷



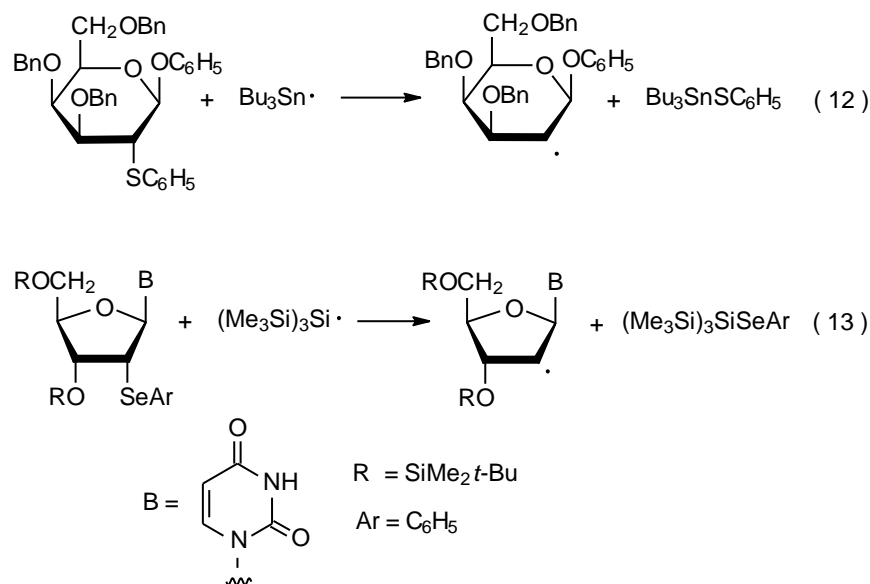
Y· = a tin- or silicon-centered radical

X = a sulfur-, selenium-, or tellurium-containing group such as SCH₃, SCH₂CH₃, SC₆H₅, SeC₆H₅, or TeC₆H₄OCH₃ (*p*)

III. Group Abstraction

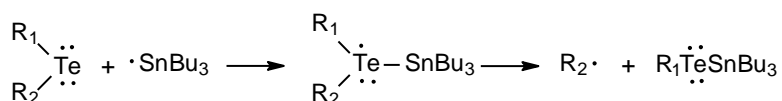
Group abstraction is possible when a group is attached to a carbon atom in a carbohydrate by a bond to a sulfur, selenium, or tellurium atom (eq 11). The abstracting radical in nearly every

instance is tin-centered (eq 12)⁸ or silicon-centered (eq 13).⁹ Although group abstraction reactions can be elementary ones, they cease to be so if an intermediate with a hypervalent atom forms (Scheme 3). (Generating a hypervalent atom causes abstraction to become a combination of radical addition and α -fragmentation.) Only rarely is a hypervalent atom believed to be involved if a sulfur or selenium atom provides the link to the carbohydrate framework.^{10,11} (An example of a noncarbohydrate, selenide reaction that appears to involve a hypervalent selenium atom is described in Chapter 8, Section III.B.) Where the connection is to a tellurium atom, computational investigations indicate that a radical with a hypervalent atom is likely form.¹⁰



Scheme 3

a reaction producing an intermediate with a hypervalent tellurium atom



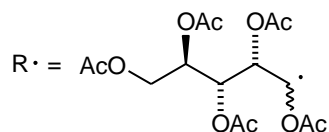
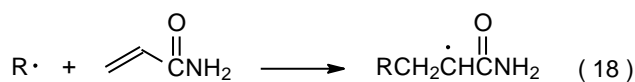
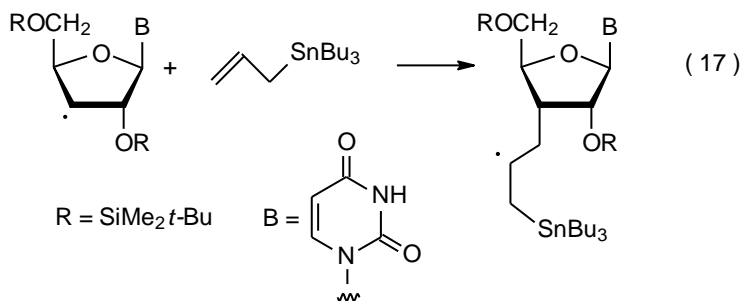
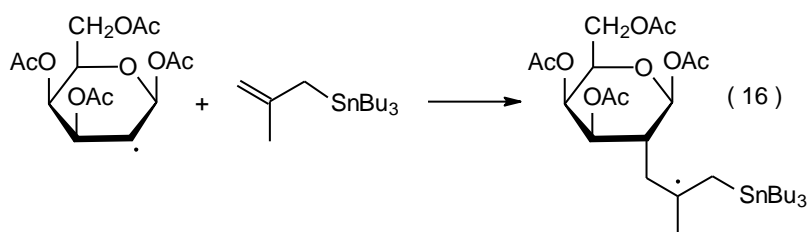
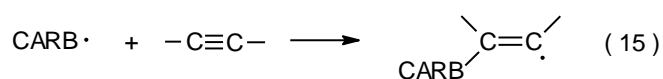
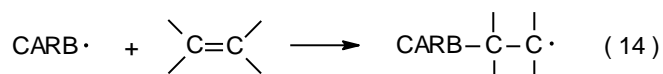
IV. Radical Addition

A. Intermolecular Reaction

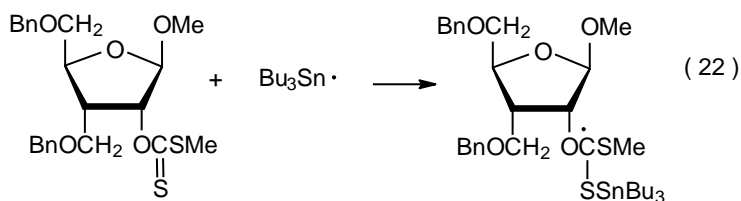
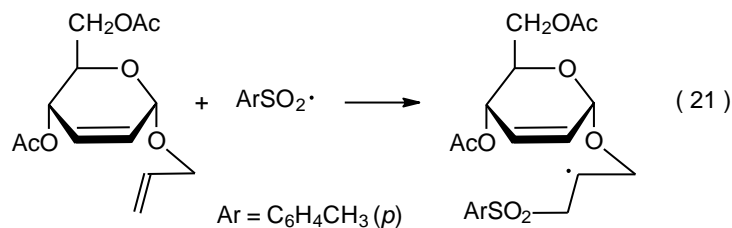
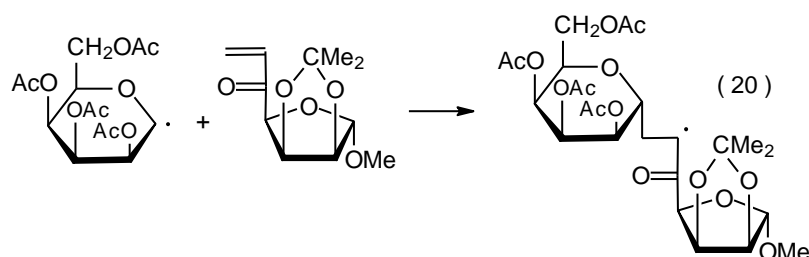
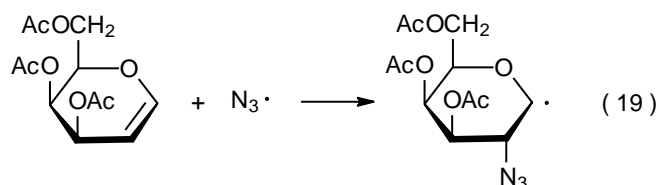
1. Addition to a Compound with Multiple Bond

Addition of a carbon-centered radical to a multiple bond in an unsaturated compound is an elementary reaction that forms a new carbon-carbon bond (eq 14 and eq 15). One way for this to happen is for a radical centered on one of the carbon atoms in a pyranoid or furanoid ring to add to an unsaturated noncarbohydrate. Examples of this type of addition are found in the reactions

shown in eq 16,¹² where a radical is centered on C-2 in a pyranoid ring, and eq 17,¹³ where the radical center is on C-3' in a furanoid ring. It is also possible to have the radical center located on a carbon atom that is in an open-chain structure (eq 18).¹⁴ Addition can involve a noncarbohydrate radical or a carbohydrate radical adding to an unsaturated carbohydrate (eq 19¹⁵ and eq 20¹⁶, respectively). When the radical and the compound to which it is adding are both carbohydrates, reaction creates complex structures quickly (eq 20).



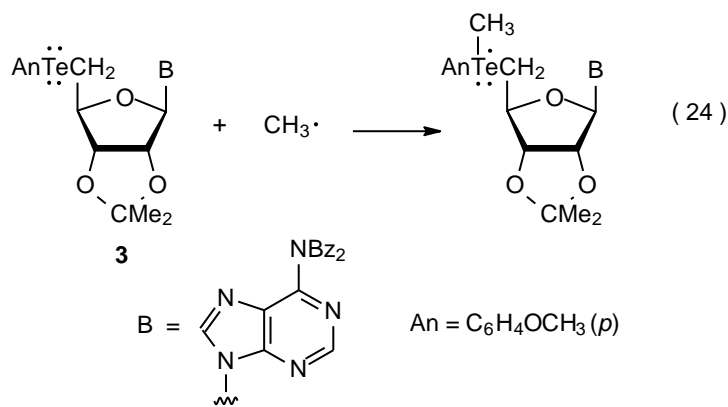
Heteroatoms play a role in radical addition when a radical centered on a nitrogen, phosphorous, silicon, sulfur, or tin atom adds to an unsaturated carbohydrate; for example, a nitrogen-centered radical is involved in the reaction shown in eq 19,¹⁵ and the adding radical in the reaction pictured in eq 21 is sulfur-centered.¹⁷ Radicals also add to unsaturated carbohydrates in which the multiple bond contains one or two heteroatoms. An example of this type of reaction is given in eq 22, where addition is to a carbon–sulfur double bond.¹⁸ Similar radical addition reactions occur with carbohydrates containing carbon–oxygen, carbon–nitrogen, and nitrogen–oxygen multiple bonds.



2. Addition That Forms a Radical with a Hypervalent Atom

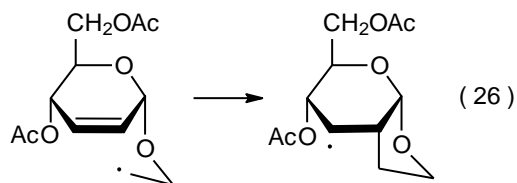
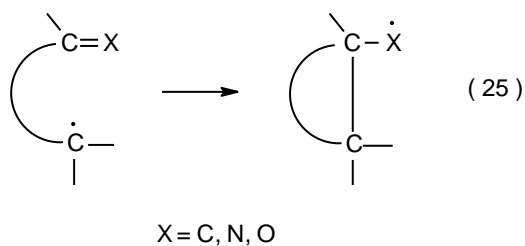
Although most addition reactions consist of a radical adding to a multiple bond, reaction that does not involve a double or triple bond also can take place. This happens when addition produces

a radical in which an atom has an expanded octet (eq 23). Such a reaction is thought to take place when a telluride, such as **3**, reacts with a methyl radical (eq 24).¹⁹



B. Intramolecular Reaction (Radical Cyclization)

Radical cyclization (eq 25) is an intramolecular version of radical addition that merits special mention due to the synthetic importance of new ring formation. Five- and six-membered rings are created most often, but larger rings also can be produced. A typical radical cyclization reaction is shown in eq 26.²⁰

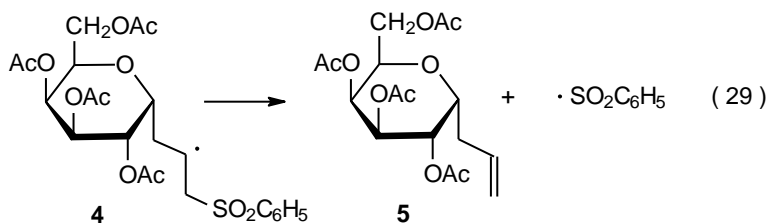
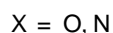
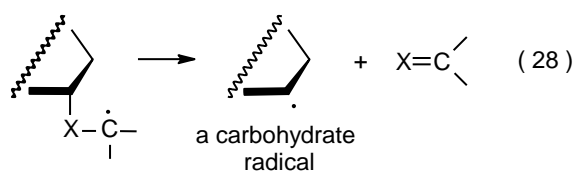
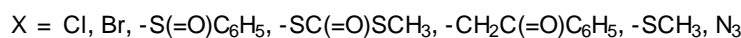
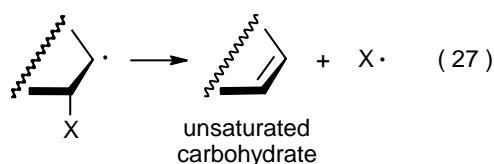


V. Fragmentation Reactions

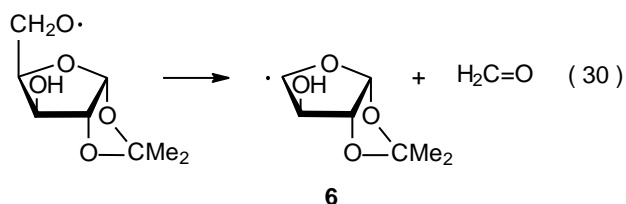
A. Homolytic β -Fragmentation

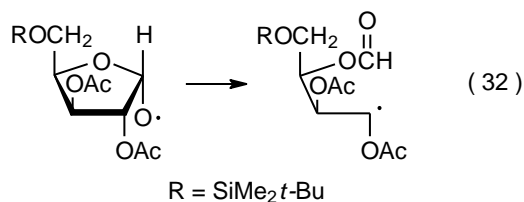
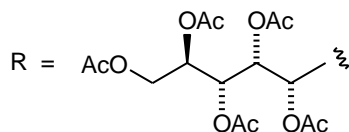
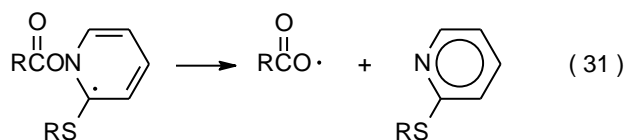
Homolytic β -fragmentation of a radical is an elementary reaction that cleaves a bond to one of the atoms adjacent to a radical center. (Other names for β -fragmentation are β -cleavage and

β -scission.) This type of reaction sometimes produces an unsaturated carbohydrate by expelling a noncarbohydrate radical (eq 27), and other times it gives a carbohydrate radical and an unsaturated noncarbohydrate (eq 28). Equation 29 illustrates the first of these possibilities with a reaction in which the radical **4** fragments to give $\text{C}_6\text{H}_5\text{SO}_2\cdot$ and the unsaturated carbohydrate **5**.²¹ Being able to form a stabilized radical such as $\text{C}_6\text{H}_5\text{SO}_2\cdot$ is an essential factor in this reaction.



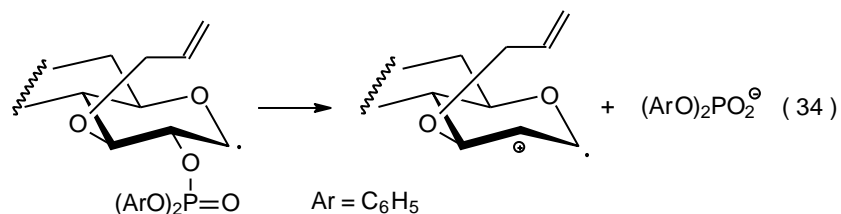
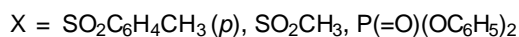
A β -fragmentation reaction producing a carbohydrate radical and an unsaturated noncarbohydrate is one driven by formation of a compound with a thermodynamically stabilized multiple bond (usually a carbon–oxygen double bond) and a radical that also is stabilized (usually by an oxygen atom attached to the radical center). The reaction shown in eq 30 fits this pattern because it produces formaldehyde and the oxygen stabilized radical **6**.²² Forming an aromatic ring is another way for providing a substantial driving force for β -fragmentation (eq 31).²³ A further option for β -fragmentation is ring opening, a possibility that presents itself when a radical is centered on an atom attached to the ring (eq 32).²⁴





B. Heterolytic β -Fragmentation

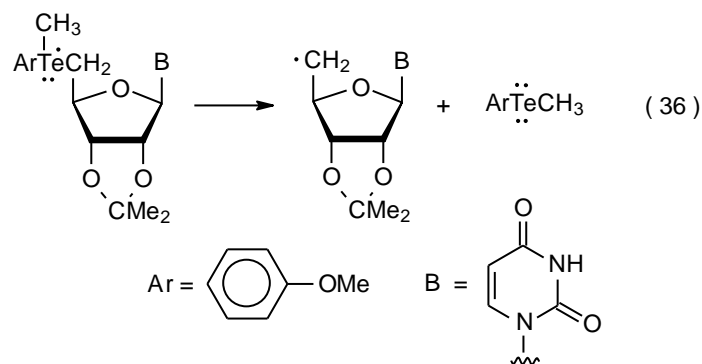
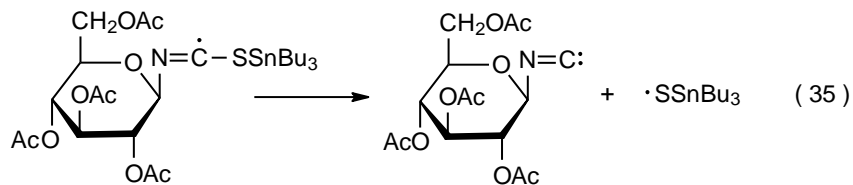
When a radical is centered on a carbon atom that has an effective nucleofuge attached to a neighboring carbon atom, the possibility exists for formation of a radical cation (eq 33). The bond from the neighboring carbon atom to the leaving group needs to be one that does not cleave homolytically with ease; otherwise, β -fragmentation producing ionic intermediates could be preempted by homolytic fragmentation. Heterolytic β -fragmentation occurs in the reaction shown in eq 34.²⁵



C. α -Fragmentation

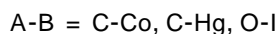
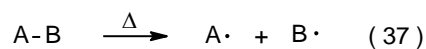
α -Fragmentation is an elementary reaction in which a bond attached to a radical center cleaves homolytically. This reaction is rare because it requires the energy-demanding step of bond breaking without the energetic compensation of bond formation. One situation in which α -fragmentation takes place is in the formation of the isonitrile and stabilized, sulfur-centered radical

shown in eq 35.²⁶ A second occurs in the fragmentation of the hypervalent radical shown in eq 36.¹⁹

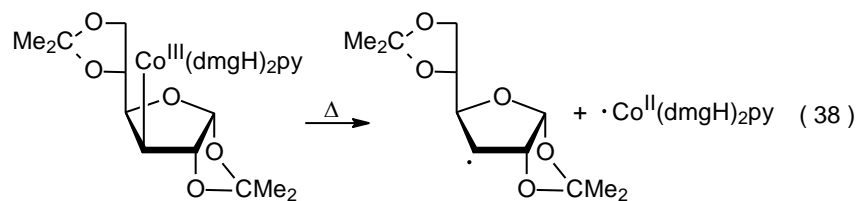


D. Bond Homolysis

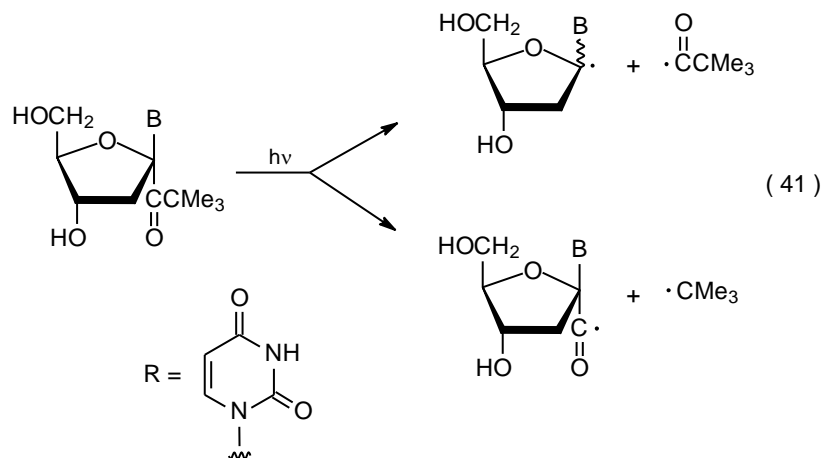
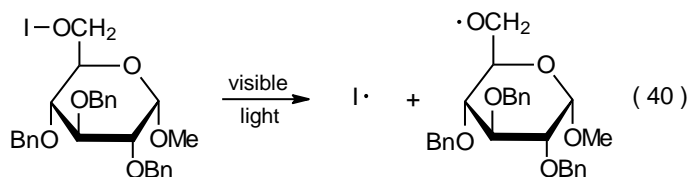
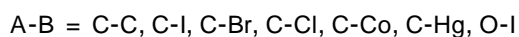
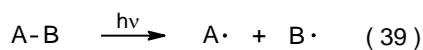
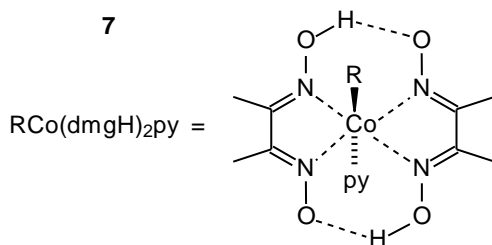
Bond homolysis either produces a pair of radicals (eq 37), or if the bond being broken is part of a ring system, a diradical. Thermal reaction cleaves the weakest bond in a molecule; thus, when the cobaloxime **7** is heated, the carbon–cobalt bond, one of the weakest covalent bonds known, breaks homolytically at temperatures well below those necessary for cleavage of other bonds in the molecule (eq 38).²⁷ This bond homolysis involves electron transfer with cobalt acting as the electron acceptor.



Photochemical reaction offers a range of possibilities for bond homolysis (eq 39). Success depends both upon a compound being able to absorb the incident light and on this light supplying sufficient energy for bond breaking. Absorption of visible light provides the energy needed to cleave weaker covalent bonds, such as the iodine–oxygen bond in the reaction shown in eq 40.²⁸ UV radiation is energetic enough to break stronger bonds, such as the carbon–carbon bonds in the reactions pictured in eq 41.²⁹



7



Unlike thermal reaction, bond breaking during a photochemical process does not necessarily cleave the weakest bond in a molecule. Selectivity in bond breaking during photolysis results from a combination of factors that control the reactivity of electronically excited molecules. In the re-

action shown in eq 41, for instance, excitation energy is quickly localized in the keto group in the substrate. This localization leads to one of the characteristic reactions of an excited aldehyde or ketone, namely, breaking the bond between the carbonyl carbon atom and one of its attached carbon atoms.³⁰

VI. Electron Transfer

A. Reactions of Carbohydrate Radicals

Transition metal complexes can act as electron transfer agents when reacting with carbohydrate radicals (eq 42 and 43). In the reaction shown in eq 44, titanium donates an electron during formation of the carbon-titanium bond between titanocene(III) chloride (Cp_2TiCl) and the pyranos-1-yl radical **8**.^{31,32} In the reaction shown in eq 45, ammonium cerium nitrate [$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$] accepts an electron from the pyranos-1-yl radical **9** to convert it into the corresponding cation.^{33,34} Other compounds that serve as electron donors in reactions with carbohydrate radicals are SmI_2 , $\text{Cr}(\text{EDTA})^{2-}$, $[\text{Ru}(\text{bpy})_3]^{2+}$, and $\text{Co}(\text{dmgH})_2\text{py}$. (The structures of the ligands in these compounds are pictured in Figure 1). In addition to $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $\text{Mn}(\text{OAc})_3$ also acts as an electron acceptor in reactions with carbohydrate radicals.



ED = an electron donor

$\text{R}\cdot$ = a carbohydrate radical

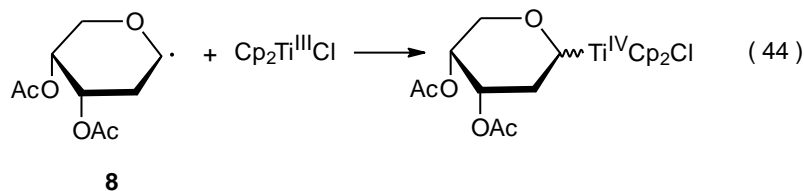
X = an integer representing oxidation state

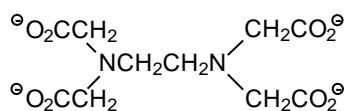
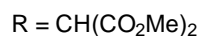
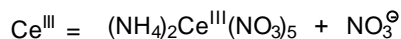
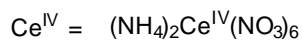
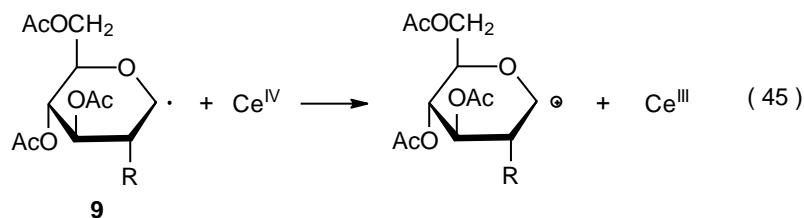


EA = an electron acceptor

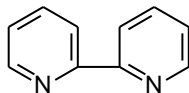
$\text{R}\cdot$ = a carbohydrate radical

X = an integer representing oxidation state





EDTA



bpy

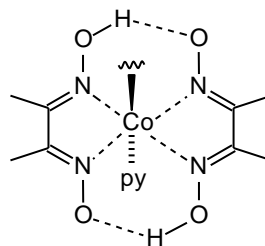
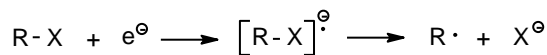
Co(dmgh)₂py

Figure 1. Ligand structures in electron donors

B. Formation of Carbohydrate Radicals

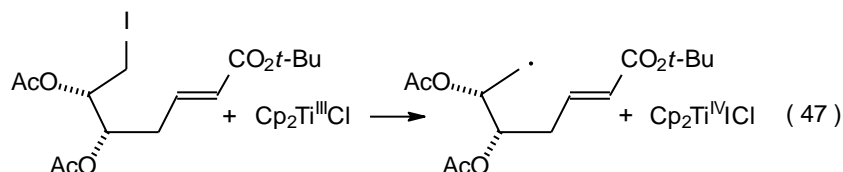
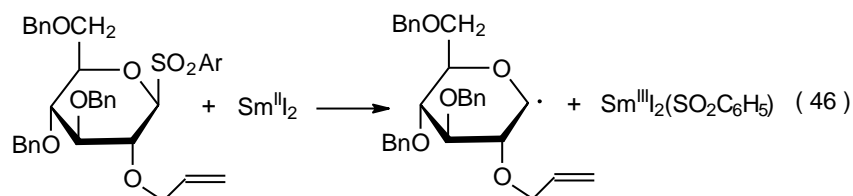
When an electron is transferred to a carbohydrate chloride, bromide, iodide, or sulfone, the resulting radical anion reacts to form a carbohydrate radical (Scheme 4). The two electron donors participating in most of these reactions are SmI_2 (eq 46)³⁵ and Cp_2TiCl (eq 47),³⁶ but other transition-metal complexes [e.g., $\text{Cr}(\text{EDTA})^{2-}$] are able to function in this capacity. Although the radical anion **10** is pictured in Scheme 4 as a discrete intermediate, in some instances cleavage of the RX bond may be simultaneous with electron transfer.

Scheme 4

**10**

R-X = a carbohydrate chloride, bromide, iodide, or sulfone

e^\ominus = an electron supplied by an electron donor



Solvated electrons, which are more reactive as electron donors than transition-metal complexes, combine with esterified carbohydrates to produce radical anions. These radical anions then expel carboxylate anions to form carbohydrate radicals (eq 48).³⁷

Reaction of an aldehyde or ketone with samarium(II) iodide produces a samarium ketyl (eq 49),³⁸ an intermediate considered to be a hybrid of structures **11-13** (Figure 2). These ketyls exhibit reactivity characteristic of carbon-centered radicals.

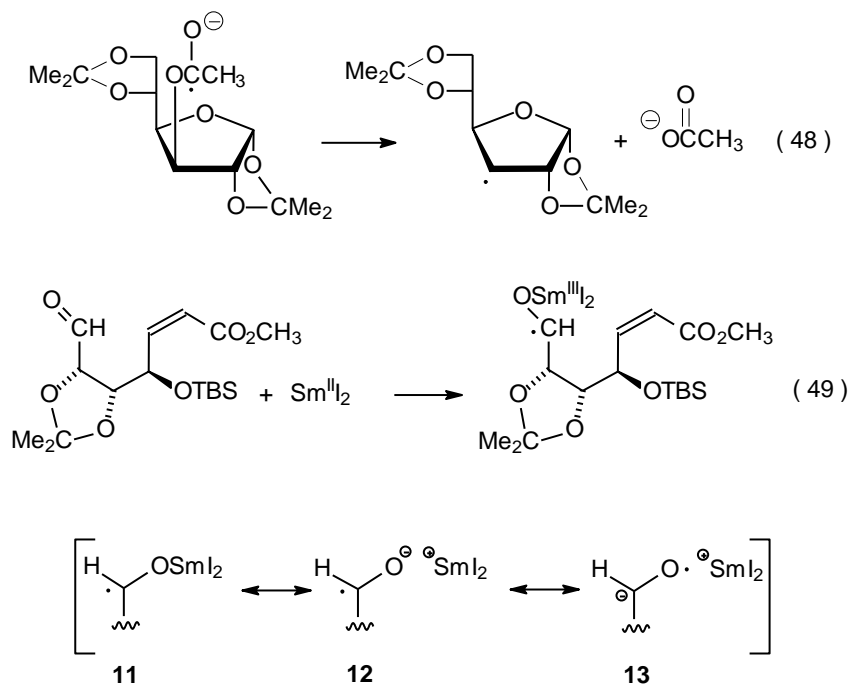
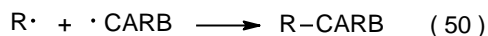


Figure 2. Resonance contributors for samarium ketyls

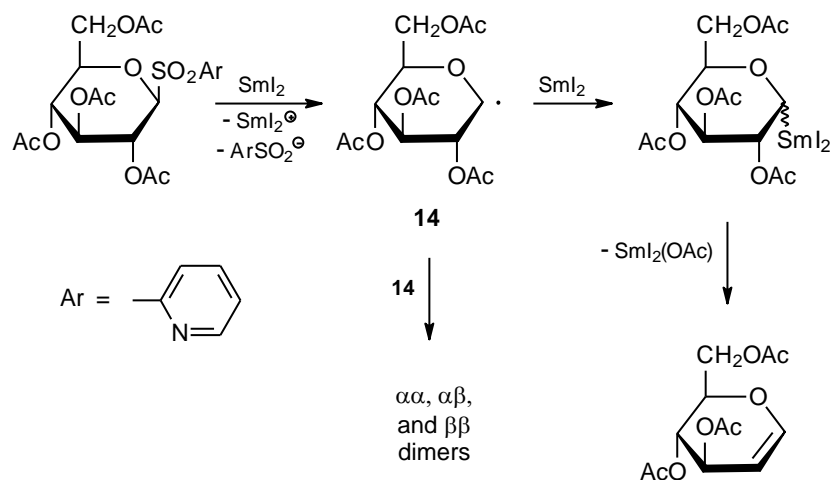
VII. Radical Combination

Radical combination involving carbohydrates takes place either by reaction between two carbohydrate radicals or between a carbohydrate and a noncarbohydrate radical (eq 50). Successful radical combination requires that the rates of competing reactions (e.g., hydrogen-atom abstraction and radical addition) be reduced to the point that radicals exist long enough in solution to combine. Under most conditions the lifetimes of typical carbohydrate radicals are too short for two of them to diffuse through solution and react. If conditions are selected to minimize competing reactions, pyranos-1-yl radicals, which are among the most stable carbohydrate radicals, exist in solution long enough to come into contact with each other and thus form dimers, although in low yield (eq 51).³⁹ If conditions are chosen that produce large numbers of radicals in a short period of time, radical concentration can be raised to the point where substantial combination takes place (Scheme 5).⁴⁰

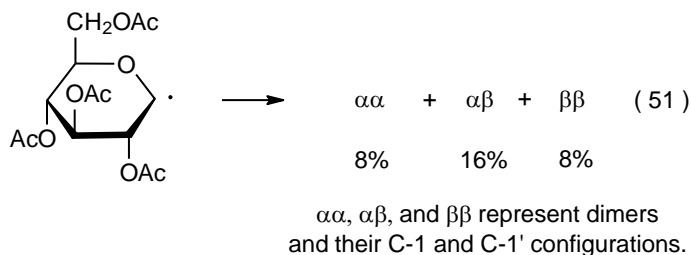


$R\cdot$ = either a carbohydrate or noncarbohydrate radical

Scheme 5

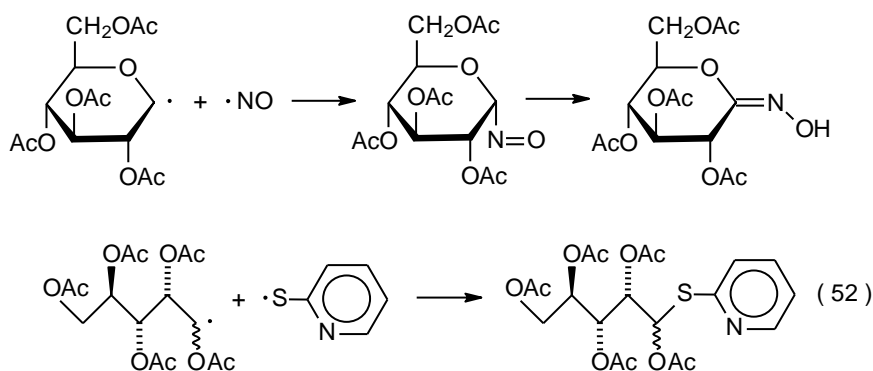


no HMPA	0%	92%
slow addition of HMPA (8 equiv) during reaction	0%	96%
HMPA (8 equiv) present at the beginning of the reaction	52%	40%



The noncarbohydrate radicals taking part in radical combination have a range of possible structures. The basic requirement in most instances is that the noncarbohydrate radical be sufficiently stable that its concentration in solution builds to the point that it will combine quickly with the more reactive carbohydrate radicals as they are produced. [Radicals with considerable stability are described as being either persistent or stable (Chapter 2, Section I.B.). The presence of such radicals provides the basis for the “persistent radical effect” discussed in Chapter 3 (Section I.B.1.c).] Noncarbohydrate participants in radical combination range from stable compounds, such as nitric oxide (Scheme 6),⁴¹ to resonance-stabilized radicals, such as the 2-pyridylthiyl radical (eq 52).²³ Electrolysis is different from most reactions because it can produce locally high enough concentrations of radicals to allow even reactive ones to combine (eq 53).⁴²

Scheme 6

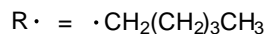
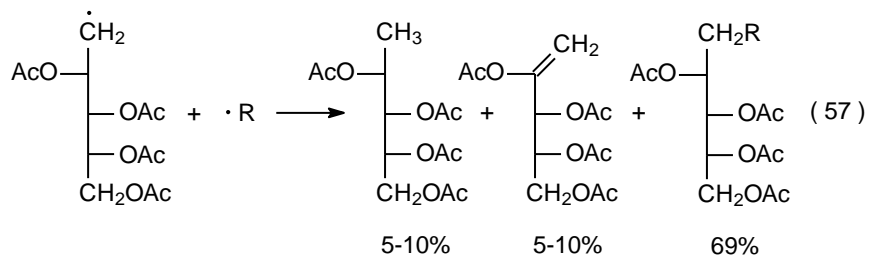
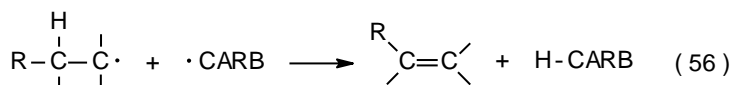
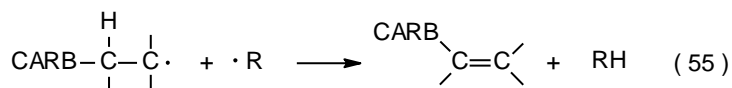
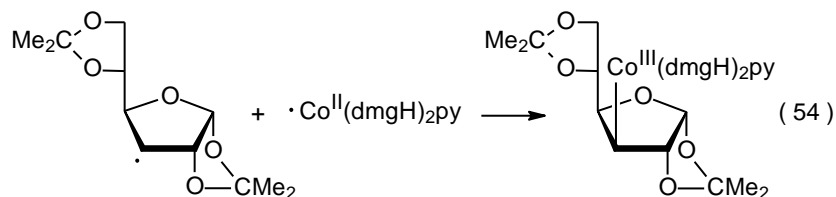
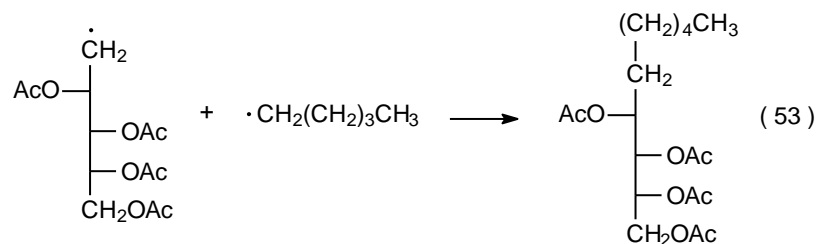


Some electron-transfer reactions between carbohydrate radicals and transition-metal complexes have a similarity to radical combination. In the reaction shown in eq 54, for instance, a change in oxidation states accompanies the combination between the carbohydrate radical and the cobalt complex.²⁷

VIII. Disproportionation

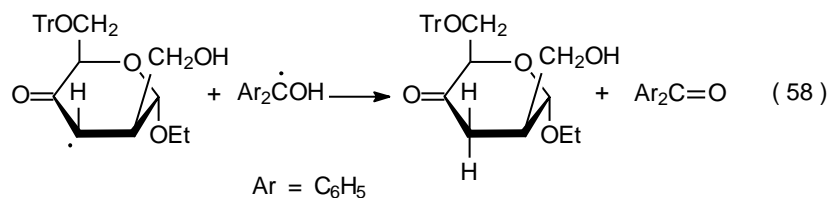
Disproportionation involving carbohydrate radicals (eq 55 and eq 56) is similar to radical combination in that most such radicals do not exist long enough in solution to come into contact

with each other before another reaction takes place. As mentioned in the previous section, one situation in which two radicals can interact is when locally high concentrations are created by electrolysis; thus, when the radicals shown in eq 57 come within bonding distance, both disproportionation (10%-20%) and radical combination (69%) take place.⁴² In contrast, disproportionation is the exclusive process in the reaction shown in eq 58 because there is considerable thermodynamic gain from forming a highly resonance-stabilized ketone while avoiding the hindrance inherent in the combination of sterically demanding radicals.⁴³



disproportionation = 10-20%

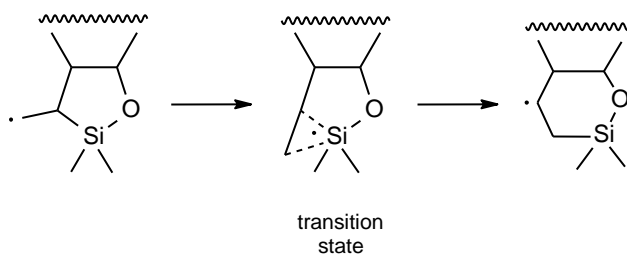
combination = 69%



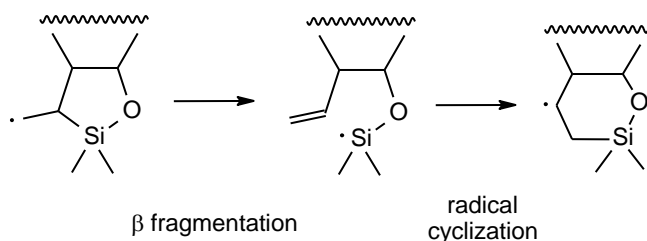
IX. Group Migration

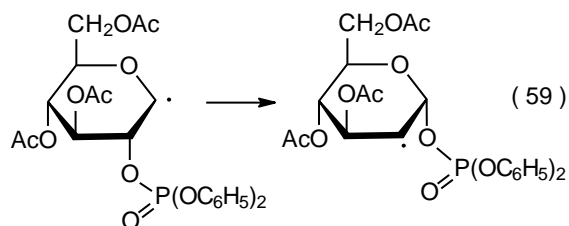
Acyl, silyl, phosphatoxy, phenyl, and cyano groups all are capable of undergoing group migration. Because in most reactions these groups are stable substituents and often act as protecting groups, migration is an event that depends not only on reaction conditions but also on the substrate having a particular type of structure. Sometimes it is unclear whether group migration is an elementary reaction or a combination of elementary reactions. The silyl group migration pictured in Scheme 7 is thought to be an elementary reaction, but it is possible that this process consists of a pair of reactions, β -fragmentation and radical cyclization (Scheme 8).⁴⁴ The group migration shown in eq 59⁴⁵ appeared at first to be an elementary reaction, but extensive investigation has shown that it consisted of heterolytic fragmentation followed by ionic recombination (Scheme 9).⁴⁶⁻⁴⁸

Scheme 7

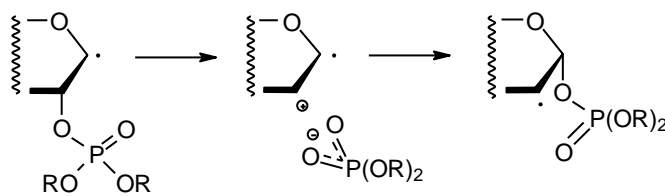


Scheme 8





Scheme 9



R = an aryl or alkyl group

X. Summary

Radical reactions are composed of sequences of elementary reactions. An elementary radical reaction is one that does not produce an intermediate. Most elementary, radical reactions consist of transformation of one radical into another, but those that create radicals from nonradicals or cause radicals to disappear also qualify. Elementary reactions are listed in a general form in Table 1. Examples of carbohydrates that undergo each type of reaction are discussed.

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